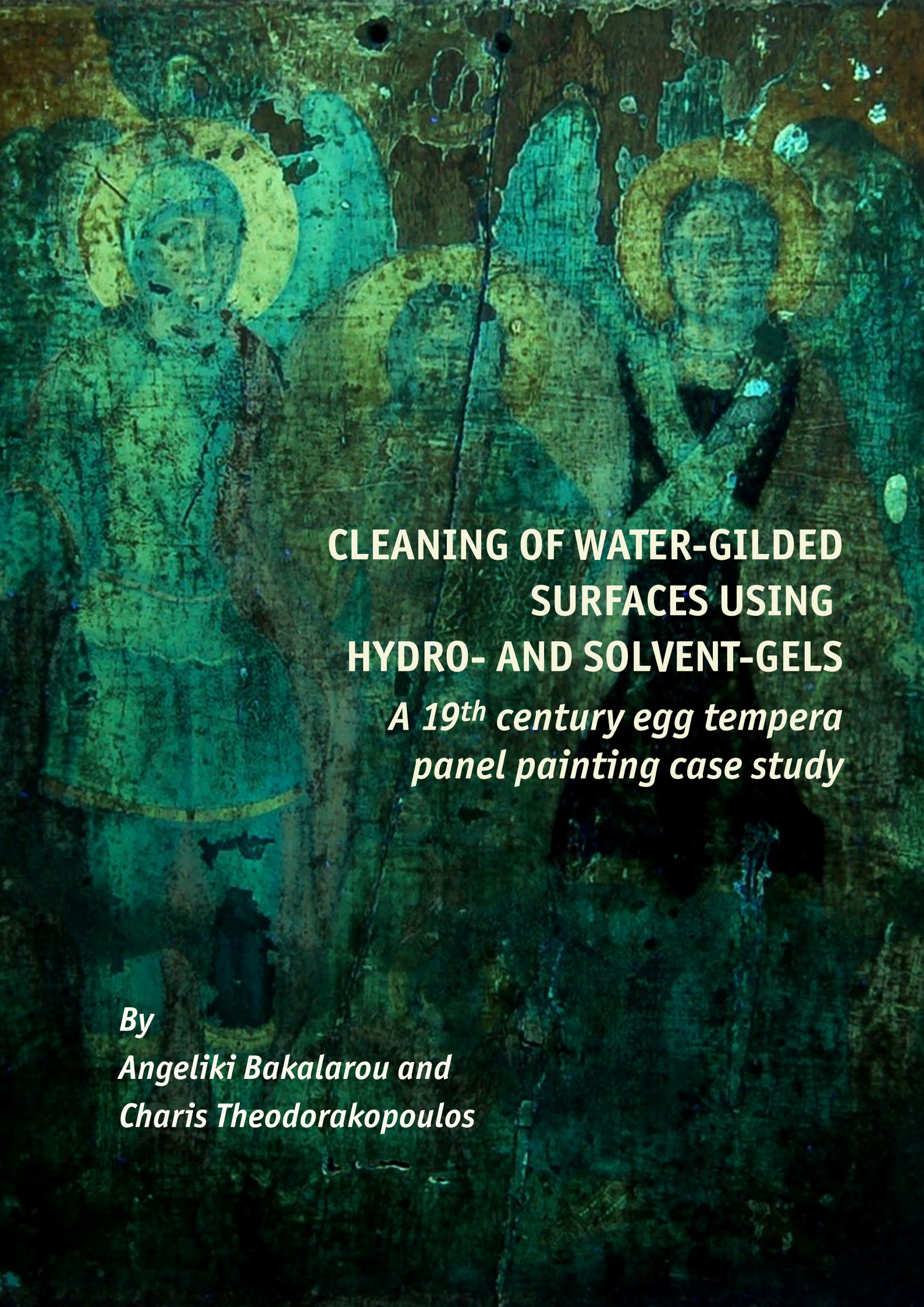

CLEANING OF WATER-GILDED SURFACES USING HYDRO- AND SOLVENT-GELS

A 19th century egg tempera panel painting case study

By
Angeliki Bakalarou and
Charis Theodorakopoulos

This paper describes the implementation of three customized gels on a 19th century panel painting for the removal of its degraded natural resin varnish from a water-gilded surface and a complex solvent-sensitive stratigraphic construction over the gilded substrate. At first, the varnish was unsoiled with a typical hydrogel that was composed of an aqueous phase buffered at pH 5.5 with sodium acetate, poly(ethylene glycol) p-(1,1,3,3-tetramethylbutyl)-phenyl ether surfactant and hydroxy-prorylmethyl cellulose. The removal of the entire aged varnish was facilitated with a microemulsion of an aqueous phase buffered at pH 8.5 with triethanolaminate, a fatty phase of a mineral spirit - benzyl alcohol solution and a polyoxy-ethylene(23)lauryl ether surfactant, altogether incorporated in a viscous gel generated from the dissolution of a polyacrylic acid in poly(oxy-1,2-ethanediyl) cocoalkylamine surfactant. The third gel, which was based on a polyacrylic acid of higher viscosity and incorporating a microemulsion of the same aqueous phase (pH 8.5) as in the second gel, and a fatty phase made of benzyl alcohol and a polyoxyethylene(23)lauryl ether surfactant, enabled the selective removal of the degraded varnish over the elaborate gilded area with a composite stratigraphy over the golden leaf. Fourier transform infrared spectroscopy and UV fluorescence imaging were employed for the analysis of the aged varnish and the monitoring of the cleaning procedure, respectively. The conservation procedure determined the effectiveness of the customized gels employed for this special implementation. The fine preservation of the water-gildings and of the complex solvent-sensitive stratigraphic construction of the painted surface was a satisfactory outcome.

Introduction

Interaction with the environment normally leads to aging and decay of the materials constituting diverse surfaces, including coatings and paints of cultural heritage masterpieces. Aging leads to discoloration of coatings, which sometimes may utterly obscure owing to deposition of soils and pollutants [1-3]. Therefore, when aged coatings begin to have a destructive impact on the appearance and the surface chemistry of an artwork, they should be removed. Removal of aged coatings may be realized upon dissolution in organic solvent blends [4,5] and/or micellar solutions [6] that should keep abuse of the underlying paints, such as swelling and leaching of volatile components from binding media, to a minimum degree [4,7-9]. In case permeation of the liquid solvents is not efficiently controlled the physical integrity of the painted surface is seriously compromised [7-9]. However, the depthwise gradients in polymerization, condensation, oxidation and consequently in the formation of insoluble matter and in polarity of aged varnishes [10-12], which are directly associated with corresponding gradients in dissolution properties [13], impede the control of liquids on varnished paints. In particular, liquid diffusion into the bulk of aged varnishes cannot be terminated once the upper and most degraded varnish layers are dissolved [13], thereby fostering permeation of the cleaning agents in the interface with the varnish substrate. Thus, cleaning procedures become precarious in case of chemical similarity of coatings and diverse components in the underlying layers.

In the presence of gilded layers, permeation of liquids during the removal of aged coatings may deteriorate both the composition of the metal alloy leafs of the gilding and the adhesives that keep the latter in place [14]. In traditional paintings, murals and icons, gilding is typically applied on a substrate, made of a mixture of hydrated aluminium silicate with various organic

sediments and iron oxides (bolo), water and egg white [15, 16]. Upon construction, this special insulating layer prevents the original ground from absorbing the adhesive of the gilding. The adhesive for joining thin metal alloy leafs with such priming layers can be either hydrophilic, made of water gelatin or natural distillation spirits, such as the polysaccharide rich 'raki' [15-17], or hydrophobic, such as linseed oil that has been treated with a siccative, traditionally lead acetate (sugar of lead) [18]. According to traditional treatises, the use of hydrophilic adhesives was typical for the gilding of original Byzantine and Post-Byzantine panel paintings [17, 19, 20]. Depending on the water or oil gilding substrates, permeation of polar or hydrocarbon liquid solutions respectively should have devastating effects given that these solvents will react with the gilding adhesive.

The use of gellants into the cleaning solutions reduces permeation into the underlying layers since all liquids are confined onto the targeted layer. The active solution within the gel network is gradually released over the surface, reducing thus the risk of swelling of the paint [21] and/or dissolution of the gilding adhesive. In addition, gels are quite versatile, provided that a great variety of aqueous solutions and/or non-polar solvents [22], microemulsions, as well as highly selective cleaning agents, such as chelators and enzymes [6, 18] can be incorporated. The increased viscosity of the gel reduces bulk diffusion of solubilized molecules within the gel liquid, while slowing the kinetics of solubilization [21]. This particular characteristic may facilitate the selective removal of a coating from a chemically similar substrate, which may be another coating, resinous paint, diverse paint media and/or gilding adhesives.

This paper presents the removal of a degraded varnish from the painted surface of a 19th century

Figure 1. The 19th century panel painting "Assembly of Archangel Michael" as received in the conservation studio. The varnish was aged and discolored and soiling deposits were scattered accross the surface of the artwork.

egg-tempera panel painting "Assembly of Archangel Michael" (Figure 1) with diverse means performed in the framework of a diploma dissertation at the Conservation Department of the Technological Educational Institute of Athens, Greece [23]. The painting, which belongs to a private collection, was a post-Byzantine icon made in egg tempera with water-gildings and a thick mastic varnish and was a subject of study, documentation and conservation treatments, from which cleaning was just a part. Cleaning of the painted surface followed an elaborate conservation treatment of the wooden panel and diverse implementations of adhesion and consolidation [23].

The painting was coated with an aged, discolored and soiled varnish, contributing to the overall obscurity of the underlying painted and gilded

surface. Moreover, there were surface scratches and losses that were in particular concentrated over the upper part of the painting. The discoloration and obscurity effects on the appearance of the underlying paint and gilding, the poor preservation state and the apparent chemical and physical damages of the varnish led to the decision to remove both the soiling and the aged varnish. Initially, the varnish over the largest part of the painting, in particular over the paints, was dissolved in organic solvents.

The cleaning procedure of the varnish over the gilded areas was implemented with customized gels. In the beginning, a hydrogel was employed to remove the soiling material from the varnish surface and a second gel to actually remove the varnish from the gilded substrate. A particular part of the gilded area with successive vulnerable layers of translucent paint and transverse brushstrokes was potentially susceptible to the cleaning agents in the former gel. Therefore, solvent-gels were synthesized with the intention of removing the degraded resin layers at the surface of the varnish and, at the same time, to protect the composite stratigraphy over the gilded substrate. Prior to the cleaning procedure, the varnish was analyzed using Fourier Transform Infrared Spectroscopy. UV fluorescence was employed to monitor the cleaning procedure.

Materials and Methods

Solvent Cleaning

The aged varnish over the painted surfaces of the painting was removed using organic solvents. At first, successive cleaning tests were performed using the following solvents and solutions: (a) low aromatic white spirit (MERCK); (b) acetone (99,5% pure, MERCK); (c) ethanol (MERCK); (d) ethanol-white spirit 1:1 solution; and (e) benzyl alcohol (puriss, Riedel-de Haën)-white spirit 1:3 solution. As shown in Figures 2 and 3, the ethanol-white spirit 1:1 blend (d) and the benzyl alcohol-white spirit 1:3 solution (e) had the best result in that they removed the coating and had the minimum visually assessed effect on the underlying paint. For the final solvent cleaning procedure, the ethanol-white spirit 1:1 solution (d) was employed to remove the aged coating from selected areas of the painted surface.

Gel Cleaning

For the comparative cleaning study of the sensitive gilded areas of the painted surface three customized gels were synthesized using the following materials: deionized water, low aromatic white spirit, benzyl alcohol, sodium hydroxide (NaOH) 1N, poly(ethylene glycol) p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100), hydroxyproryl methyl cellulose (HPMC), glacial acetic acid (CH_3COOH), triethanolamine (TEA), hydrochloric acid (HCl) 1N, a polyacrylic acid (PAA) with 416 acrylic monomers (Carbopol 934), poly(oxy-1,2-ethanediyl) cocoalkylamine (Ethomeen C/25) and polyoxyethylene(23)lauryl ether (Brij 35). All the materials were supplied by Acros Organics except for sodium hydroxide, supplied by MERCK. The materials were weighted with an OHAUS Scout Pro SPU202 analytical scale and the solutions were stirred at room temperature with a VELP SCIENTIFICA ARE Heating Magnetic Stirrer. The pH of buffer solutions was measured with a XENON portable PH 122E pH-meter.

Gel A was a hydrogel composed of an aqueous phase, Triton X-100 and HPMC (95.60% v/v, 0.57% v/v and 3.83% w/v respectively in a solution of 100 ml). The aqueous phase was glacial CH_3COOH in deionized water (0.50% v/v), which was buffered to pH 5.5 with the dropwise addition of 1N

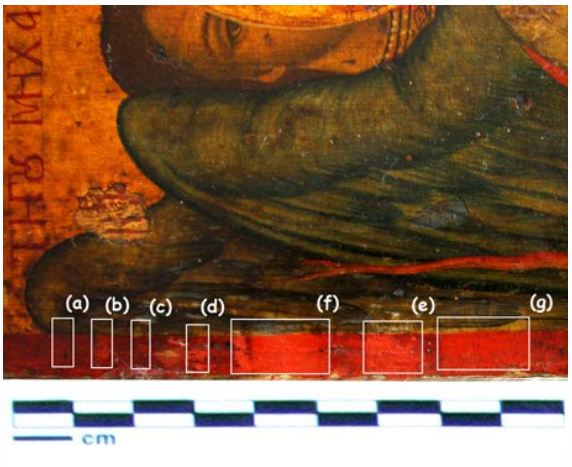

Figure 2. The dissolution tests employed at the surface of the painting indicate that solution (d) (ethyl alcohol-white spirit 1:1) was able to remove the coating with minimal effects on the underlying paint. This solution was employed to remove the aged coating from selected areas of the painted surface. The areas marked (f) and (g) are the dissolution tests for gels B and C, respectively.

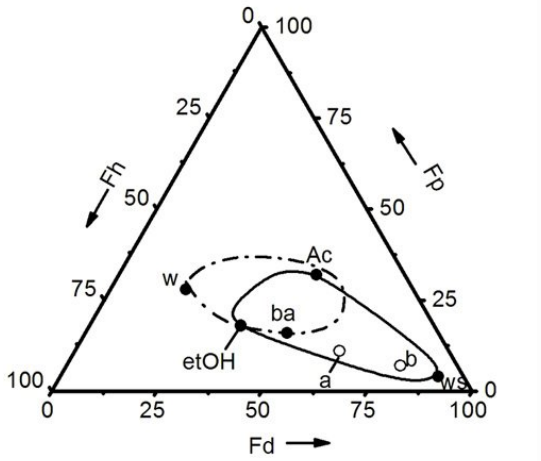

Figure 3. The ternary Teas solubility plot showing all the tested solvents (●): acetone (Ac), benzyl alcohol (ba), white spirit (ws), ethanol (etOH), distilled water (w), and the solutions (○): (a) etOH-ws 1:1, (b) ba-ws (1:3), with the solubilization limits of both resin mastic (--) and proteinaceous materials (-·-), including egg yolk and polysaccharides [34]. The graph indicates that neither of the solutions would affect the water gilding of the panel painting.

NaOH solution. Gel A was employed to remove the soiling material from the surface of the coating. After use, rinsing was performed with the buffer solution.

Gel B was based on a microemulsion that was synthesized of an aqueous phase, a viscous PAA gel and a fatty phase (1.4%, 70.6% and 28.0% v/v, respectively in a solution of 50 ml). The aqueous phase was TEA in deionized water (3.33% v/v), which was buffered to pH 8.5 with the dropwise addition of 1N HCl solution. The PAA gel was a mixture of Carbopol 934 in Ethomeen C/25 (5.0% w/v), deionized water and white spirit (17.8%, 10.7% and 71.5% v/v respectively). The fatty phase, which was a 10% w/v blend of Brij 35 in a white spirit - benzyl alcohol 3:1 solution, and the aqueous phase were vigorously shaken together until complete homogeneity. The solution was left to calm and form two separate phases. The upper phase was collected and added to the viscous PAA gel to form gel B.

Gel C was another solvent-gel based on a microemulsion that was composed of the same aqueous phase and the same viscous PAA gel as in gel B and an altered fatty phase, which was 20% w/v Brij 35 in benzyl alcohol, (1.6%, 82.0% and 16.4% v/v, respectively in a solution of 50 ml). These components were brought into homogeneity by first mixing both the aqueous and fatty phases before the addition of the PAA gel. Solvent-gels B and C were employed to remove the aged coating from the gilded areas of the painted surface. All gels were applied to the painted surface using a 00 brush. They were allowed to remain for a few seconds (5-10 sec) and removed from the surface using a dry cotton swab. Clearing of the surface after implementation of gels B and C was performed using low aromatic white spirit as suggested elsewhere [6].

Fourier Transform Infrared Spectroscopy

The absorption infrared spectrum of the coating of the panel painting was recorded with a Perkin

Elmer Spectrum GX Fourier Transform Infrared (FTIR) spectroscopy system. A small sample of the coating was taken with the aid of a scalpel blade. The sample was then mixed (c. 10% w/w) with potassium bromide (KBr) and pulverized in an agate mortar. The powdered sample was accordingly inserted in a standard cylinder die system (SpecAc) and pressed (SpecAc pressing apparatus) with 10 tons/cm^2 for approximately 60 seconds into a KBr disc. The spectra were obtained in the transmission mode within the mid-IR range (4000-400 cm^{-1}) after 20 scans at a resolution of 4 cm^{-1}. Spectral analysis was carried out using the Spectrum software package by Perkin-Elmer.

UV Fluorescence Imaging

The surface was examined with a Waldmann W Diagnosis Light TypHLL 264 device equipped with two ultraviolet fluorescent lamps (Philips TL 4W/08 F4T5/BLB), emitting between 315-408 nm (peak at 368 nm). The surface was photographed with a digital Nikon D50 camera, with 6.24 Megapixels analysis (6.1 effective Megapixels) and 18-55 mm normal type lens AF-SDX Nikkor 18-55 mm f/3.5-5.6 GEDII (Ø 52 mm). A circular polarizer Cinko (Cinko Circular Polarizing Filter) and a UV Kodak Wratten 2E (75 mm) filter were employed to cut off reflectance and the corresponding UV wavelengths, respectively. The camera was adjusted with the following parameters: f/5.6 aperture, 25 seconds shutter speed and 100 ISO sensor sensitivity. The camera was fitted on a tripod in order to keep the lens parallel to the painted surface during the shooting procedure.

Figure 4. UV fluorescent image of the coated surface showed a green-yellow emission that indicated the presence of an aged natural resin varnish. The non-fluorescent dark areas and back spots indicated the presence of soiling depositions.

Results

Under UV fluorescent irradiation, the varnish of the painting had a green-yellow emission (Figure 4), indicating the presence of an aged natural resin film on the surface of the painting [24]. FTIR analysis (Figure 5) confirmed the presence of aged resin mastic as the main component of the varnish [25, 26]. The evident intense absorbance around 1710 cm^{-1}, where the C=O carbonyl stretching vibration of aldehydes, ketones, and carboxylic acids of the triterpenoid molecules is detected, demonstrated the rather advanced oxidation state of the varnish. In addition, UV fluorescence provided evidence for the presence of the deposited soils across the surface that blocked the efficient absorbance of the UV light from the underlying varnish and appeared as non-fluorescent dark areas and black spots (Figure 4).

The principal cleaning procedure that was designed to liven up the painted surface was the solvent-based removal of the aged varnish over the painted surface (Figure 6) and the selective removal of

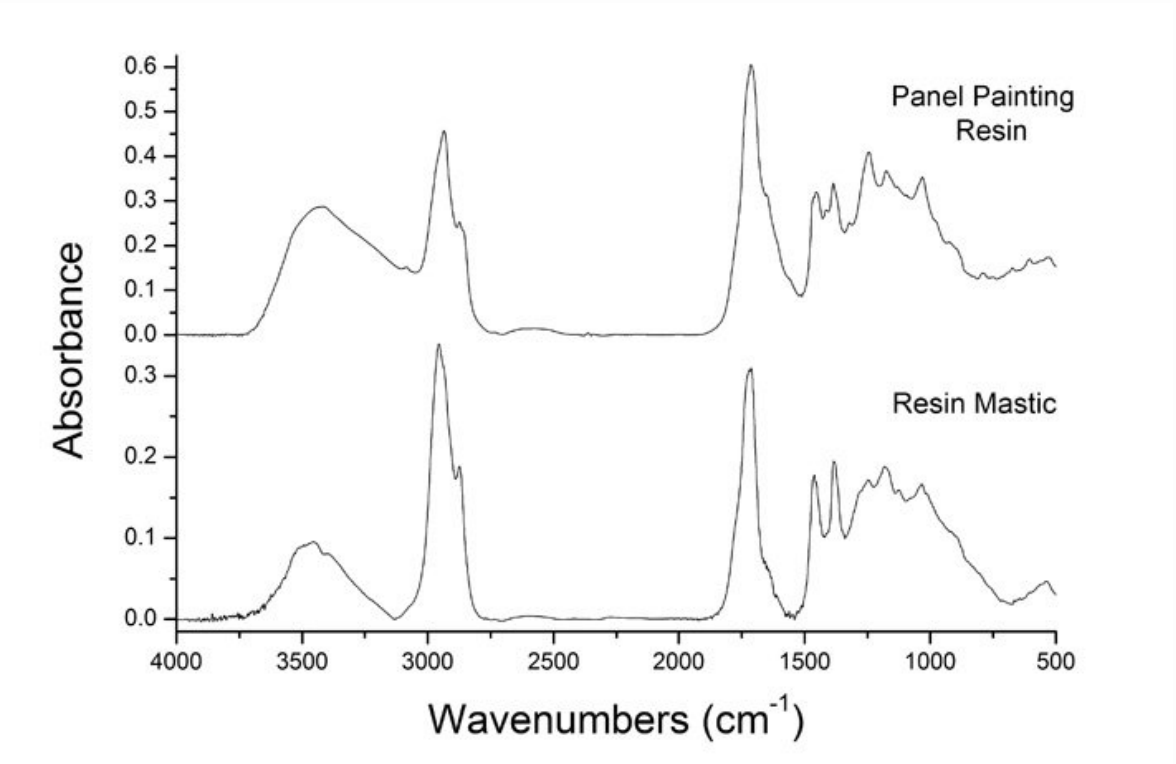

Figure 5. The FTIR absorbance of the varnish of the panel painting compares well with that of resin mastic.

pollutants and varnish using customized gels over the gilded surface. At first, a few dissolution tests were performed using a short list of solvents, which were capable to dissolve resin mastic with negligible or no swelling effects on the underlying paint [26], which according to traditional treatises was expected to be egg tempera [17]. These tests demonstrated that a 50% (v/v) solution of ethanol in mineral spirits was efficient for the cleaning process (Figures 2 and 3). Indeed, the varnish was readily dissolved over the painted surface that was left in a visually-assessed satisfactory preservation state (Figure 7). The same solution was tested for the cleaning of a selected area over the gilded surface at the upper right corner of the painting (Figure 8a). Observation of the former surface showed a general dimness, microcracks, localized detachments and some minute losses of the golden alloy leaf (Figure 8b), possibly due to both partial dissolution of the gilding adhesive and/or stress cracking effects [27].

In conclusion, there was a great risk of deteriorating the painting after solvent cleaning, in particular of the gilded areas. Additionally, some finest and elaborate parts of the surface, such as the area of the clothing of the right figure, depicting Archangel Gabriel, which was constructed using an elaborate stratigraphy over a gilded area, was considered to be quite sensitive for solvent cleaning. Definitely, the fine and translucent paint brushstrokes over the golden leaf were to be preserved. Therefore, varnish removal from the remaining gilded areas was performed with customized gels, which provide advanced selectivity during the cleaning procedure [6].

Gel cleaning of the gilded areas was attempted in two stages, by the synthesis of two types of gels to selectively remove the soiling depositions at first and then the aged varnish respectively. In particular, soiling removal from the surface of the coating was enabled with gel A that was a

Figure 6. The blue-stripped pattern demonstrates the areas of the painted surface where the aged varnish was removed with the ethyl alcohol-white spirit (1:1) solution.

Figure 7. The painted surface after solvent cleaning.

Figure 8. Detail of the gilded area (a) where the ethyl alcohol-white spirit (1:1) solution was tested before cleaning. Solvent cleaning resulted in a general dimness, microcracks, localized detachments and some minute losses of the golden leaf (b).

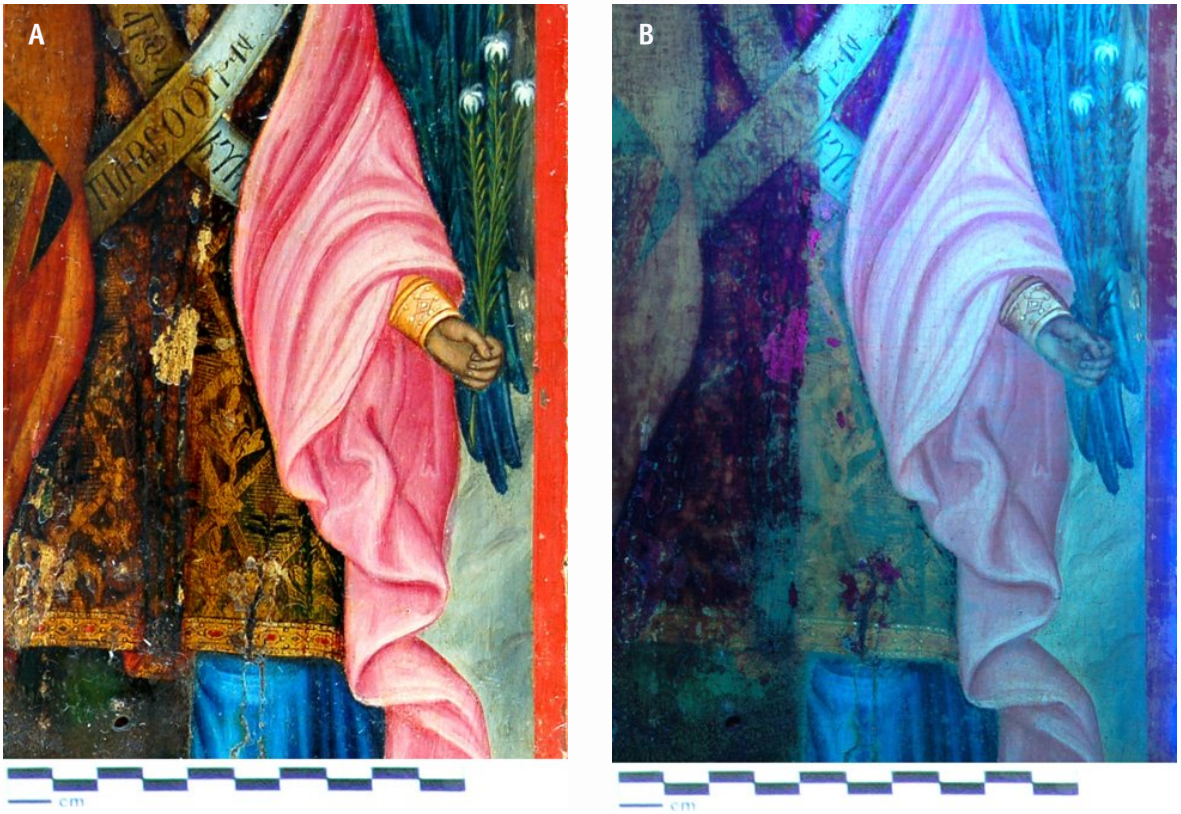

Figure 9. Visible (a) and UV fluorescence (b) images of the gilded part of the clothing of Archangel Gabriel as unsoiling with the HPMC hydrogel (gel A) was in progress. The left part of the gilded surface demonstrates the obscurity problems introduced by the soiled and discolored varnish, while at the right part the improvement of the area appearance is obvious. The successful soiling removal is confirmed by UV fluorescence (b). Note that varnish of the surrounding painted surface was removed earlier with organic solvents.

hydrogel buffered to pH 5.5. This gel enabled the removal of the depositions that obscured both varnish and paint (Figure 9). It is possible that the cleaning procedure might have had some minimal hydrolytic effects on the varnish. Nevertheless, the revealed varnish remained discolored and affected the aesthetical homogeneity between the underlying gilded surface and the cleaned painted surface, which in the largest extent was uncoated after the solvent-based varnish removal.

Therefore, it was decided to selectively remove the aged and discolored varnish over the gilded areas of the painting. A viscous PAA microemulsion solvent-gel (gel B) was employed to minimize diffusion of the cleaning agents into the bulk of the aged varnish [6]. The pH of the aqueous phase of the microemulsion was raised to 8.5 to breakdown via ionization the majority of the oxidized triterpenic acids of the mastic coating [28] and to encapsulate the varnish fragments into micelles [6, 18]. As shown in Figure 2, gel B (test area f) did not have the expected selectivity and entirely removed the aged varnish. Possibly, implementation of the rather low-selective gel B on the finest and elaborate gilded parts at the clothing of Archangel Gabriel would have had devastating effects.

Therefore, a more viscous and more polar PAA microemulsion solvent-gel (gel C) was composed. As demonstrated in Figures 2 (test area g), 10 and 11, gel C removed the surface layers of the

Figure 10. Detail of a selected gilded area during the partial removal of the varnish layer: a) implementation of the highly viscous PAA solvent-gel (gel C) on the area; b) the same area after cleaning with gel C.

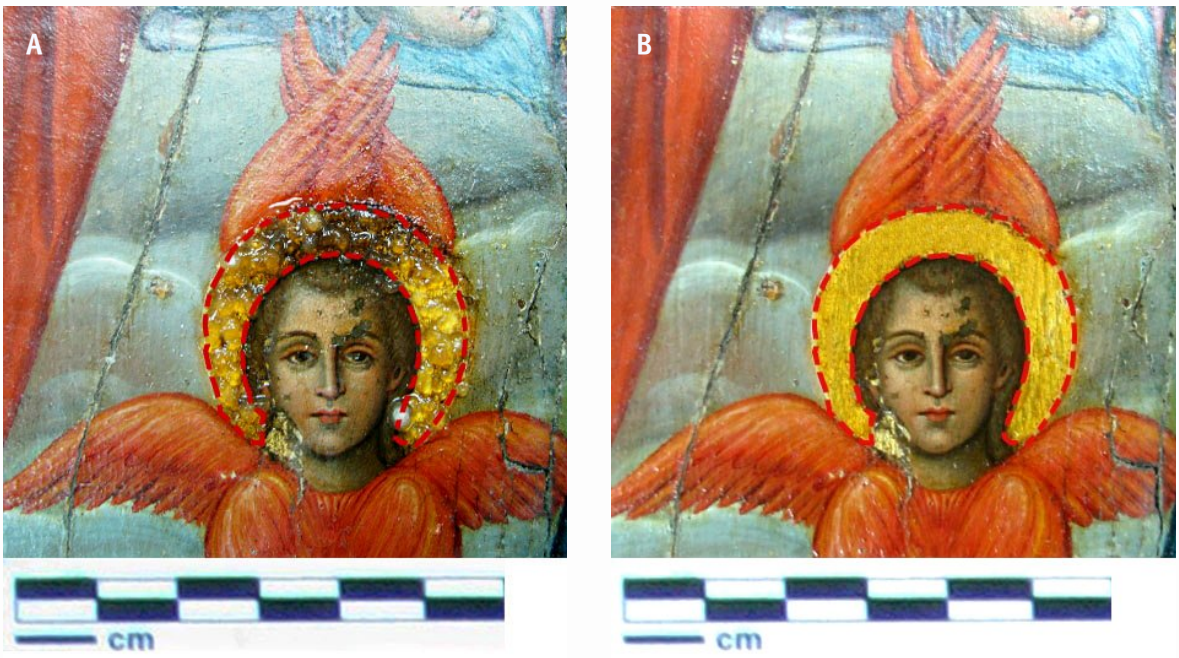

Figure 11. Detail of a selected gilded area during the partial removal of the varnish layer: a) implementation of the highly viscous PAA solvent-gel (gel C) on the area; b) the same area after cleaning with gel C.

Figure 12. Detail of the gilded part of the clothing of Archangel Gabriel after cleaning with gel C. Although there are no substantial changes captured in comparison with the same painted gildings after unsoiling with gel A (see Figure 9), the particular elaborate area appears brighter. Note that the varnish of the surrounding painted surface was removed earlier with organic solvents.

varnish successfully. This was quite obvious during the process, as the removed resin entities from the surface were yellowish. The cleaning result of the particular elaborate gilded area of the clothing of Archangel Gabriel is indicative of this observation, given that all layers above the gilding and below the aged varnish were efficiently preserved and the area appeared cleaner after gel implementation (Figures 12 and 13). Unfortunately, photographs did not capture substantial changes of the visual appearance in particular of the painted gildings, in comparison with the previous stage (after unsoiling), because both the aged varnish and the gilded surface were yellow.

Discussion

This document is an account of traditional and modern cleaning procedures employed on a typical 19th century hagiographic panel painting. The soiling material was removed from the varnish surface using custom-made gels. Solvents and gels were then employed to remove the aged varnish from the painting. Aiming at the optimum selectivity, the cleaning procedure was designed to remove the soiling material first and the aged varnish in a following step. This strategy would reduce precipitation of the hard soiling particulates onto the painted and gilded surfaces. Accordingly, the possibility of mechanical wear of the artwork surfaces due to creeping of and friction with the soils was eliminated.

The soiling material was removed from the varnish surface using an HPMC hydrogel (gel A) that contained an acetic acid/sodium acetate buffer (pH 5.5) and a non-ionic surfactant Triton X-100 (Figure 9). Similar hydrogels that have been employed to remove soils from varnish and paint surfaces are discussed elsewhere [6, 21, 22, 25, 29, 30]. HMPC increases the viscosity of aqueous solutions and converts them into hydrogels. In this case, the aqueous solution intended to ionize the polar groups of the triterpenic carboxyl acids in the aged mastic resin [4], leading to swelling of the cross-linked, condensed and polymerized network of the varnish [12]. This procedure facilitates the release of the embedded soiling particulates. Upon oxidative aging, natural resins like mastic form weakly acidic acids that exhibit a negative base-10 logarithm of their dissociation constants (pKas) in an approximate range of 6.5-7.5 [6, 31]. The ionization process of the carboxylic acid group of aged natural resins begins at a pH of a point lower and utterly completes at a pH of a point higher than their pKa values [6]. Thus, the acidity of gel A was adjusted at pH 5.5, which is a

Figure 13. The painting after completion of the cleaning procedures.

point lower than the pKa of most triterpenoid acids in mastic [6, 28]. The surfactant Triton X-100 was added into the solution in order to decrease the surface tension of the water, as well as to act as a detergent factor to the solution. The former property optimized wetting of the varnish surface from the hydrogel, while the latter aided at the encapsulation of the dispersed soils into micelles.

Removal of the aged varnish was carried out using two methods: at first solvent-based removal over the painted surfaces [23] and then gel-based

cleaning over the gilded areas which is discussed below. Typically, significant parts of 19th century Greek-Orthodox hagiographic panel paintings were water gilded, based on traditional treatises of the Byzantine era [15-17]. These treatises recommend adhesion of golden leaves on specially primed surfaces with "raki", which is composed of polysaccharides and promotes an effective although weak adhesion. In order to preserve the adhesion of the golden leaves on the surface, any cleaning agents must not dissolve the polysaccharide-based medium. Polysaccharides are very polar [18] and are therefore susceptible to polar solvents such as alcohols, ketones and water. The ternary Teas solubility plot [32] of polysaccharide supports this observation [33], although the limits of dissolution of such adhesives could be broader than that demonstrated by Horie [34]. As shown in Figure 3, it was expected that working on the gilded surface with a solvent blend of ethanol in white spirit (50% v/v) would be quite safe, but the actual implementation showed that the golden leaf surface was defected (Figure 8). Gel cleaning provided some confidence especially for minimizing the risks of defects in the gilded areas, provided that liquid permeation from the gel is eliminated.

A viscous microemulsion solvent-gel was composed based on the mixture of an aqueous phase (TEA, deionized water, HCl, pH 8.5), a viscous PAA gel (Carbopol 934 in Ethomeen C/25, deionized water and white spirit) and a fatty phase (Brij 35 in a white spirit - benzyl alcohol 1:3 solution) (gel B). The adjustment of the acidity of the solution to pH 8.5, which is at least one unit over the maximum pKa≈7.5 [6, 31] of most oxidized triterpenic acids in natural resins [28], intended the dissociation and encapsulation of the varnish fragments into micelles [6, 18]. The benzyl alcohol - white spirit 1:3 solution used in the fatty phase of gel B showed good results at the preliminary dissolution tests of the aged varnish over the painted surfaces of the painting (Figure 2). Also, benzyl alcohol as a solvent combines both alcohol and aromatic solvent properties and demonstrates a balance in polarity, making it quite effective on dissolving materials that combine both aromatic and hydrogen properties, like natural resins [6-8, 18]. The addition of the non-polar white spirit solvent provided some control of the polarity of the cleaning agents. Based on the Teas solubility diagram (Figure 3), gel B would not affect the gilding because the benzyl alcohol-white spirit 1:3 solution that was enclosed in the fatty phase appears outside the dissolution limits of polysaccharide media [33]. Brij 35, which was used in the fatty phase solution, is a non-ionic surfactant and therefore compatible with the weak polyacrylic acid Carbopol 934 and the weak base Ethomeen C/25, employed to increase the viscosity of the gel. Finally, Brij 35, benzyl alcohol, as well as the Carbopol 934/ Ethomeen C/25 gel are dissolved in white spirit and therefore can be rinsed off the surface [6]. Despite the high concentration of the viscous PAA polymer (70.6% v/v) in gel B, the concentration of the fatty phase (28% v/v), containing the benzyl alcohol-white spirit 1:3 blend, sufficed to unleash the solubility power of the solvent solution and to entirely dissolve the aged varnish (Figure 2). This is normally an acceptable result because of the exceptional cleaning efficiency but not for this particular case where sensitive fine and translucent paint layers over the water gilded surface were to be protected. For this case, the intention was to partially remove the aged varnish and hence an even more viscous solvent-gel (gel C) was synthesized.

Gel C was based on a microemulsion gel that was composed of the same aqueous phase and the same viscous PAA gel as in gel B and a different fatty phase (Brij 35 in benzyl alcohol). Gel C had two important differences in comparison to gel B.

At first, the concentration of the PAA polymer was increased in gel C (82.0% v/v vs 70.6% v/v in gel B), which made it more viscous than gel B and therefore allowed the former to remain longer on the surface of the varnish. Secondly, white spirit was not included into the fatty phase as in gel B. Thus, the microemulsion in gel C had an increased polarity providing a more drastic dissolution of the polar groups at the surface of the aged varnish. Given the aging-induced oxidation and polarity gradients [10-12], both degrees of polarity and oxidation are higher at the surface and reduced at the bulk of the aged coating. Subsequently, it was assumed that the aforementioned properties of gel C would suffice to both restrict diffusion of the limited cleaning agents into the bulk of the aged coating and efficiently dissolve the highly degraded surface layers of the varnish. As demonstrated in Figures 10 to 12, gel C was able to successfully remove the surface layers of the varnish.

A Comment on Gel Residues

Recently, a lot of concern has been expressed with regards to the residues of cleaning gels on painted surfaces [35]. Residues may vary depending on the variety and the concentration of the diverse polymers and cleaning agents employed. In accordance with the materials used for the gel formulations described herein, there are specific warnings on the residues of PAA-Ethomeen gels, which may leave Ethomeen surfactant and polyacrylate fragments heterogeneously distributed across the surface [35]. In case a surface is left uncoated after gel implementation, Ethomeen residues degrade to acetaldehyde and glyoxal by UV-initiated decomposition that in the long ran evaporate, although a lightly cross-linked layer of stable polyacrylates may remain on the surface [35]. These concerns may be compromised by the fact that in the case described herein, the gilded substrate was hydrophilic due to polysaccharide-based adhesive of the golden alloy leaf. This suggests that attraction of water gildings with particular entities such as long hydrocarbon chains of polyacrylates and hydrocarbon tails of surfactants, is minimal compared to that of lipophilic paint media. In addition, highly concentrated gel residues have been observed in areas with relatively high porosity and pronounced surface micro-topography, as is the case of paint [35]. In contrast, gildings, which are smooth and non-porous surfaces, should normally retain fewer residues, in particular at limited areas with microcracks and fissures of the golden leaf. The contribution of such residues as they age on the surface is a matter of future research. Despite these concerns, the selectivity obtained with the implementation of gels must not be overlooked.

Conclusions

The implementation of three customized gels for the cleaning of a 19th century panel painting was described in the present article. After identifying the varnish by FTIR as being mastic, three gels were developed to interact with it. The varnish was first unsoiled with a typical HPMC hydrogel with a non-ionic surfactant Triton X-100 and sodium acetate buffer to regulate acidity at pH 5.5. The removal of the entire aged varnish down to the interface with the gilded surface was facilitated with an Ethomeen (C/25)-PAA (Carbopol 934) solvent-gel that contained a microemulsion of an aqueous phase buffered at pH 8.5 with triethanolaminate and a fatty phase of a mineral spirit - benzyl alcohol solution and Brij 35. A third PAA solvent-gel of a higher viscosity incorporating a microemulsion of the same aqueous phase (pH 8.5), as in the second gel, and a fatty phase made of benzyl alcohol and Brij 35 enabled the selective removal of the upper parts of the degraded varnish

over an elaborate solvent-sensitive gilded area. FTIR spectroscopy and UV fluorescence imaging were employed for the analysis of the aged varnish and the monitoring of the cleaning procedure respectively. The experience gained herein demonstrated that the interaction between the surface layers of a resin varnish and a strong solvent is possible through viscous gels, with minimal risks since diffusion of the solvents through the layers is limited. The effectiveness of the customized gels was demonstrated by the fine preservation state of both paint and gilded surfaces after the cleaning processes. Conservators are advised to pay attention to the case-specific character of the surfaces to be cleaned, in terms of constituent materials and their degradation state. A sound scientific support is highly recommended in order to optimize the interaction of such surfaces with the diverse materials that are employed to synthesize a gel.

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ANGELIKI BAKALAROU

Conservator-restorer
Contact: ang.bakalarou@gmail.com

Angeliki Bakalarou is a conservator of antiquities and works of art, graduated from the Conservation Department at Technological Educational Institute of Athens, Greece in 2011. In the framework of the TEI-A educational program she gained professional experience in the conservation dept of Byzantine Museum for a six-month period in 2009, where she was involved in conservation routines on panel paintings and post-byzantine icons. Her senior student dissertation at TEI-A that involved advanced conservation treatments, including cleaning implementations on painted, lacquered and gilded surfaces, gained the highest qualification. Currently she is attending the MA Postgraduate Programme at Camberwell College of Arts, London UK.

CHARIS THEODORAKOPOULOS

Conservation scientist
Contact: ctheodlos@teiath.gr

Charis Theodorakopoulos received a PhD in 2004 at the Royal College of Art, London in collaboration with the Molecular Painting Research Group in FOM-Institute for Atomic and Molecular Physics (AMOLF), Amsterdam and the Foundation of Research and Technology-Hellas (IESL/FORTH), Heraklion, Greece. After a four-year post-doctoral research fellowship at University of London, Birkbeck College in the Conservation Science Group, he joined the TEI-A Conservation Department, as an associate scientist/assistant professor since 2008. In 2011, he joined the IESL/FORTH Bio-Organic Materials Chemistry Laboratory (BOMCLab). In parallel, he works as a freelance consultant both for artist materials and cultural heritage conservation workshops.

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Rua Germano Vigdigal, 17, r/c D
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www.e-conservationline.com

All correspondence to:
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